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(54) Fuel cell integrated with steam reformer.

(57) A H₂-air fuel cell integrated with a steam reformer is disclosed wherein a superheated water/methanol mixture is fed to a catalytic reformer to provide a continuous supply of hydrogen to the fuel cell, the gases exhausted from the anode of the fuel cell providing the thermal energy, via combustion, for superheating the water/methanol mixture.

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FUEL CELL INTEGRATED WITH STEAM REFORMERBACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to a fuel cell system integrated to utilize hydrogen produced by steam reforming of methanol as well as a method and apparatus for producing a hydrogen containing gas by steam reforming of methanol. This reformer is particularly suitable for use in an integrated fuel cell system for producing electric power from methanol.

2. The Prior Art

Fuel cells generate electricity through galvanic combustion of fuel process gas with oxidant process gas. Typically oxidant gas can be obtained from the fuel cell environment with little, if any, processing. The fuel process gas, on the other hand, is usually hydrogen and its generation requires processing of other fuels such as methanol. Direct oxidation of fuels such as methanol in fuel cells at practical current densities with acceptable catalyst loadings is not as economically attractive as conversion of methanol fuel to a hydrogen-rich mixture of gases via steam reforming and subsequent electrochemical conversion of the hydrogen-rich fuel stream to direct current in the fuel cell.

In addition, during recent years, industrial requirements for hydrogen have increased rapidly, and a variety of processes for the manufacture of hydrogen have been developed to fill this need. Large quantities of hydrogen are used, for example, in synthesis of ammonia; for catalytic hydrogenation, for example, of oils to solid fats; in petroleum processes such as hydrofining; and as a fuel, e.g. in missiles and in fuel cells for the generation of electricity.

A very attractive fuel cell system currently undergoing commercial consideration is the reformed

methanol fuel-phosphoric acid electrolyte-air system.

Primary advantages of phosphoric acid electrolyte (85 wt. %) include ability to operate with fuel and ambient air containing CO₂, ability to operate with a thin matrix electrolyte (no liquid circulation) and chemical stability of the electrolyte over the operating temperature of the cell, e.g. 180-200°C.

The fuel cell itself is only part of the overall system, and other components of the system, e.g., generation of hydrogen fuel, are likewise important in terms of overall system size and cost effectiveness.

In one method used by the art to produce hydrogen by steam reforming, a methanol and steam feedstock is passed through catalyst filled tubes disposed within a reactor or reformer which is shaped much like a conventional shell and tube heat exchanger except that the tubes contain catalysts. In these reactors, hot gases (typically combustion products) are passed through the shell of the heat exchanger while the methanol and water vapor is passed through the tubes. Thus, the heat required for the endothermic catalytic reforming reaction taking place within the tubes at about 300° C must pass through the wall of the tube. In these prior art processes, the mixture of methanol and steam is converted to a gaseous stream consisting primarily of hydrogen (about 68%) and CO₂ (about 21.7%), CO (about 1.5%) and H₂O (about 8.8%). In order to improve the thermal and chemical efficiency of such reactors, efforts have been directed to improve the uniformity of heat distribution in the tubes within the reactor to secure high chemical conversion of fuel into hydrogen and maintain catalyst bed temperature within certain limits (>700°F) in order to avoid premature catalyst aging while minimizing the amount of energy used to produce each unit of hydrogen containing gas.

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For the most efficient operation of the steam reforming reaction, large surface areas are required to transfer the heat from the combusted gases to the tubes. In reformers presently used for steam reforming, small diameter reaction tubes are clustered closely together in the furnace so that heat transfer from the combusting gases in the reactor into the catalyst packed tubes is optimized.

The use of a plurality of tubes to accomplish heat transfer contributes to the large size and high cost of the reformer. A second drawback to such reformers is that the heat for the steam reforming process is provided indirectly by means of heat transfer through tube walls. This inefficient heat transfer has a detrimental effect in fuel cell systems in which the reformer and the fuel cell are fully integrated, i.e the combustion gases for the reforming reaction are derived from the fuel cell exhaust since the shell side heat transfer coefficient between the hot gas and the tube is characteristically low and hence, the rate of reaction is limited primarily by the rate of heat transfer. This problem is particularly severe at the reactor entrance as the rate of the endothermic reaction is very high, and thus, the amount of heat required is very high while the shell side heat transfer coefficient is often low as the mechanical design of typical reactors often allows the gases in the shell to be relatively stagnant near the tube entrances. This leads to a drop in the overall efficiency as a large portion of each reactor tube operates at an undesirably low temperature. Thus, in order to effect complete conversion, the reformer must be relatively large and expensive since, at the inlet of the reformer, it is impossible, because of the highly endothermic nature of the reaction, to supply enough heat to the surface area of the reformer tubes so there tends to be a large

decrease in reactant temperature in the area adjacent the inlet.

It is the primary object of the present invention to provide a novel process and apparatus for the production of hydrogen by steam reforming of methanol that can be accomplished with a thermally efficient reformer of reduced size and cost which can be integrated with a fuel cell power system or used as a stand alone hydrogen generator.

According to the present invention, production of hydrogen by steam reforming of methanol or other hydrocarbon fuels is accomplished in a reformer of substantially reduced size by superheating a gaseous mixture of water and methanol to a temperature of about 700° to about 1100°F. and then passing the superheated gaseous mixture over a catalyst bed contained in a reformer. At least a substantial portion of the heat for the endothermic steam reforming reaction is provided by the sensible heat in the super heated steam/methanol stream augmented by heat transferred through the tube wall depending on the overall system considerations. The concept of providing a substantial portion of the heat for the endothermic reforming reaction by sensible heat in the superheated steam/methanol stream is referred to hence forth as "direct heating."

Direct heating is of considerable advantage as it largely overcomes the problems encountered with reaction rates being limited by the rate of heat transfer through the tube wall especially near the reformer entrance and thus, for a given conversion, the reactor may be smaller, more efficient and less expensive. As compared to the prior art, high steam to methanol ratios are required for direct heated reformers, typically in the range of from 1 to as high as 10. The relatively large amounts of steam passed through the bed continuously clean the catalyst by removing ethanol and suppressing production of carbon

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monoxide and retard catalyst poisoning thereby enhancing catalyst stability.

Direct heated reformers are particularly suitable for integration with fuel cells as the heat and fuel values contained in exhaust stream from each component can be utilized in the other. Hydrogen contained in the exhaust gas from the fuel cell anode may be burned to superheat the methanol/water mixture being fed to the reformer. In some embodiments, once the reactor is warmed up, the entire fuel requirements for the system are provided by the methanol being fed to the reformer.

As a result of direct heating of the reformer feed gases augmenting indirect heat transfer through the wall of the reactor, a shell-and-multiple tube reactor arrangement or other means of increasing the heat transfer surface is not always required and the complexity and overall volume of the reformer can be substantially reduced. Another aspect of this invention is based upon the realization that an efficient practical integrated reformer-fuel cell system and process can be achieved by using a superheater, an essentially adiabatic methanol reformer and a fuel cell wherein the various exhaust streams from the components are utilized with other components of the system. In this system, the water to methanol ratio and temperature of the stream leaving the superheater are of such values that substantially all (at least about 75%, preferably 90%) of the heat required for the endothermic reforming reaction is contained within the reaction stream itself and, at most, only a small portion of the heat required for reforming is supplied through the wall of the reforming reactor. In addition to the reformer size reduction achieved by the use of direct heating, a further reduction in reactor size is achieved by use of an essentially adiabatic reactor since it is highly advantageous to integrate the direct heating steam

reforming process with a fuel cell to form a fuel cell system whereby a continuous supply of hydrogen could be provided to the fuel cell from an essentially adiabatic steam reformer, the gases exhausted from the anode of the fuel cell providing thermal energy via combustion for superheating the water/methanol mixture.

It is therefore a primary object of the present invention to efficiently integrate a fuel cell with the steam reforming process to provide a thermochemical process for producing electrical energy in which the heat required for the endothermic reforming reaction is contained substantially completely within the stream fed to the reformer which produces hydrogen for a fuel cell so that a compact and efficient system may be obtained.

The above object of the invention is achieved in accordance with the fuel cell system of the present invention comprised of a heat exchanger, a burner, an adiabatic steam reformer and a fuel cell wherein a superheated mixture of water and methanol is first converted by an essentially adiabatic endothermic catalytic reforming reaction to hydrogen. The hydrogen, generated in the reformer, is directed to the fuel electrode of the fuel cell, and air is directed to the oxygen electrode to effect an electrochemical reaction to produce electricity and gaseous reaction products. A portion of the exhaust gases from the fuel electrode is combustible as it contains unreacted hydrogen. Furthermore, it is desirable to withdraw this portion of gas from the fuel cell to maintain a hydrogen-rich stream in the fuel cell thus optimizing fuel cell operation in accordance with the present state of the fuel cell art. The combustible gas exhausted from the fuel electrode is burned in the burner, the exhaust of which is fed to the heat exchanger to supply heat for superheating the water/methanol mixture fed to the reformer. Even though large amounts of water are used in the system and thus

more heat is required to vaporize and preheat these methanol water mixtures containing large amounts of water, the heat generated can be effectively recovered and used in the system and process of the present invention. Further, parasitic power requirements are decreased, and the low concentration of carbon monoxide in the reformat should lead to improved fuel cell efficiency and extended fuel cell life, so the net methanol demand remains essentially constant or may decrease slightly (around 20%). Thus, the net energy production is at lease substantially equivalent to that obtained using mixtures containing lesser amounts of water.

DETAILED DESCRIPTION OF THE INVENTION

Having set forth its general nature, the invention will best be understood from the subsequent more detailed description wherein reference will be made to the accompanying drawings which illustrate systems suitable for practicing the present invention.

Reference is now made to Figure 1 of the drawings which schematically illustrates a flow scheme in accordance with this invention of the steam reforming of methanol for the production of hydrogen therefrom. As illustrated in Figure 1, a water and methanol feedstock having a water/methanol mole ratio ranging from about 1.0 to about 10.0, preferably about 2.0 to about 9.0, and more preferably about 2.5 to about 4.0, is supplied via conduit 10 to vaporizer 11 wherein the water/methanol feed supplied thereto is heated to a temperature of about 200 to about 500°F to convert the feedstock into a gaseous mixture. The hot gaseous steam/methanol stream then exits the vaporizer via line 12 and is supplied to superheater coil 13 contained in burner 14. The gaseous mixture contained in coil 13 is superheated to a temperature of about 700 to about 1100°F, and preferably about 850°F to about 1000° F, the fuel for heating the

mixture being supplied to burner 14 via conduit 16 together with an oxidizing gas such as air or another oxygen containing gas via conduit 15. When the reforming system is integrated with a fuel cell, the fuel burned in the burner 13 includes unreacted hydrogen gas exhausted from the anode side of the fuel cell which undergoes combustion with an oxidizing gas such as air or oxygen. In one embodiment of the invention, the temperature and composition of the methanol/steam mixture leaving the superheater are such that at most only minimal additional heat will be required to obtain essentially complete conversion of the methanol contained therein. Table I sets forth the variation in weight hourly space velocity (and thereby reactor size) obtained by varying the methanol/water mole ratio of 4.5 to 9.0.

Table I

					Projected WHSV*
					for 99.8%
					Methanol
<u>WHSV</u>	<u>H₂O/MeOH</u>	<u>Inlet Temp.</u>	<u>% Conversion</u>	<u>Conversion</u>	
1.5	4.5	900°F	84.6%	0.45	
1.5	9.0	900°F	96.2%	0.789	

* Weight hourly space velocity in units of gm methanol feed/gm catalyst/hr.

For purposes of the present invention, H₂O to MeOH mole ratios of from about 2.5 to about 4.5 are preferred at temperatures of from about 900° to about 1100°F.

Gases resulting from the combustion reaction may exit burner 14 via line 14A to reformer 18 in contact with the outside of the catalyst bed. This would provide some additional heat to the reforming reaction and prevent heat loss from reactor 18, thereby reducing the

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size of reactor 18. In the embodiment in which all of the heat for the reforming reaction is supplied by preheating of the reformer feed gases, reformer 18 can be constructed in the form of a single tube having a length to diameter (aspect) ratio of less than 10:1, preferably less than 8:1, more preferably less than 6:1, most preferably from about 2:1 to about 6:1. The superheated steam/methanol gaseous mixture exits superheater coil 13 at a temperature of 850 to 1000°F and a pressure of 14.7 to 150 psia via line 17 and is supplied to reformer 18 at the desired superheated temperature and pressure.

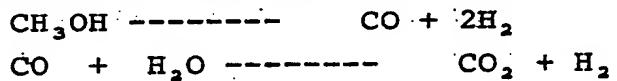
In another embodiment wherein a large portion of the heat for the endothermic reforming reaction passes through the tube wall, the reformer illustrated in Figure 3 having a multiplicity of tubes may be used.

The superheated steam/methanol gaseous mixture is reformed as it passes through a tube packed with a suitable catalyst (not shown) contained in reformer 18. The steam reforming catalyst is typically a metal or metal oxide supported on an inert ceramic material. For example, a suitable steam reforming catalyst is zinc oxide (e.g about 30 to 65% by weight zinc)/chromium oxide (about 5 to 35% by weight chromium) or a zinc oxide (about 5 to 20% by weight zinc)/copper oxide (about 15 to 40% by weight copper) combination supported on alumina (about 15 to 50% by weight).

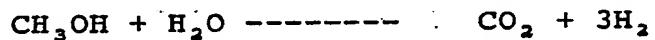
It has been determined that steam reforming in accordance with the practice of the present invention is optimized and heating is accomplished more readily when the reformer tube is divided into two catalyst sections, i.e. a first section from the inlet to the reactor tube to an intermediate position in the reactor tube containing a catalyst which has relatively low activity but good resistance to high temperatures, such as zinc/chromium oxides and a second section extending from the end of the first section to the outlet area of the

reactor tube containing a high activity catalyst such as copper/zinc oxides. Alternatively, the low activity, high temperature resistant catalyst may be used by itself.

In order to accommodate the endothermicity of the reforming reaction, heat is provided to reformer 18 as the sensible heat contained in the superheated gases. Thus, when methanol vapors and steam contact a catalyst such as a combination of zinc oxide and copper oxide at 500 to 900°F at atmospheric or higher pressure, methanol in effect decomposes to carbon monoxide and hydrogen while the carbon monoxide and steam correspondingly react according to the well known water gas shift reaction to form carbon dioxide and hydrogen as set forth below:



so that the overall reaction taking place in reformer 18 is:



Thus, within reformer 18, methanol and steam react endothermically at high temperature to produce a gaseous product consisting primarily of steam, hydrogen and carbon dioxide which is recovered from reactor 18 and supplied via conduit 19 either to condenser means 20, wherein most of the water is removed from the gaseous hydrogen/carbon dioxide mixture by cooling the gaseous mixture to condense the water or directly via line 19a to the fuel cell. Where condensing means are used, water exits condenser 20 via line 21 and a gaseous mixture of hydrogen and carbon dioxide exits condenser 20 via line 22 and in this state may be supplied for direct utilization at the fuel side or anode of a fuel cell. If desired, the hydrogen/carbon dioxide mixture may be further fractionated, by means not shown, to recover separated quantities of hydrogen and carbon dioxide.

The introduction of superheated steam and methanol of the preferred temperatures and compositions into the catalyst bed in the reforming system, illustrated in Figure 1, permits the reforming apparatus to be made more compact, at least substantially narrower and with fewer reaction tubes than an apparatus relying on a standard feed of water and methanol which would require a large number of reaction tubes for producing an equivalent reforming effect. For many applications, the reformer can, if desired, be constructed in the form of a single tube. In a typical hydrogen production process using the reforming system illustrated in Figure 1, methanol is passed with steam over a catalyst at pressure typically ranging from 14.7 to 150 psia and temperatures in the range of about 850 to about 1000°F. Typical steam to methanol mole ratios (H_2O /carbon) are in the range of about 2.5:1 to about 4:1. The conversion of methanol may be effected in one pass over the catalyst bed contained in the reformer.

Figure 1 as described above, schematically shows small scale equipment for carrying out the methanol steam reforming process of the present invention. The foregoing principles are readily applicable to the design of large scale equipment for the production of hydrogen in accordance with well known techniques.

The system shown in Figure 1 for steam reforming methanol into hydrogen is particularly adapted for use in, and can be efficiently integrated with, a fuel cell system.

Figures 2, 3, 4 and 5 illustrate an assembly integrating a steam reformer, combustor, superheater and fuel cell air preheater in one compact unit. As illustrated in Figure 2, cylindrical housing 100 and defines combustion chamber 102 mounted adjacent to shell 104 having central duct 106 passing therethrough.

Hydrogen supply duct 101 and methanol supply duct 103 lead into combustion chamber 102 to provide fuel for vaporizing and superheating the methanol water mixture. Air preheater tube 107 passes through combustion chamber 102 below superheater coils 108 disposed within combustion chamber 102 and operably connected to methanol supply/heater tube 110 passing through central duct 106 in shell 104. Methanol supply/heater tube 110 exits into methanol inlet plenum 112 opening into reformer tubes 114 leading to hydrogen exhaust plenum 118 having hydrogen exhaust ports 120 operably connected thereto. As illustrated in Figures 3 and 4, air preheater 107 is disposed below methanol steamfeed superheater coils 108 in combustion chamber 102 and is operably connected to the cathode of the fuel cell (not shown). In operation, a fuel-air mixture (such as hydrogen from the anode of a fuel cell) is introduced into combustion chamber 102 through combustor inlet duct 101, the exhaust from combustion chamber 102 flows cocurrently along methanol supply/heater tube 110 over reformer tubes 114, past baffles 128 and 130, then exits through combustor exhaust ports 132 and 134. Air for the cathode of the fuel cell enters air inlet port 136, passes through air preheater 107 situated in combustion chamber 102 and exits through air exhaust port 138. The methanol water mixture to be reformed enters through methanol inlet port 140, is superheated in superheater coils 108 located in combustion chamber 102, then is directed cocurrently upward with the combustion exhaust through methanol supply/heater tube 110 into methanol inlet plenum 112, thence through reformer tubes 114 and exits through hydrogen exhaust plenum 118 and hydrogen exhaust ports 120.

In figure 6, integrated heater reformer unit 201 is substantially the same as the integrated reformer unit illustrated in Figures 2 and 5 having combustion chamber

202 formed therein opening into central duct 206. Superheater coil 208 disposed within combustion chamber 202 is operably connected to methanol supply/heater tube 210 disposed within central duct 206 and opens into methanol intake plenum 212 joined by reformer tubes 214 to hydrogen exhaust plenum 218 having hydrogen exhaust line 220 connected thereto leading to condenser 241 and thence to anode 242 of fuel cell 244. Hydrogen contained in the exhaust from anode 242 of fuel cell 244 is removed by means not shown and is fed to combustion chamber 202 through line 280 and burner 227. Fuel cell coolant circulates through fuel cell 244 removing excess heat therefrom, line 248 conducts the fuel cell coolant to evaporator 250 which vaporizes the water methanol feed supplied to superheater 208 through line 252. Air preheater coil 224, disposed within combustion chamber 202, heats air entering through inlet 254 connected to line 256 then returns it to cathode chamber 258 of fuel cell 244 through heat exchanges 260 and means not shown. Heat exchanger 260 also serves to preheat combustion air passing through line 286 and burner 227. Methanol and water mix to be reformed into hydrogen and converted in fuel cell 244 is stored in tank 264 connected to evaporator 250 by line 265. Fuel cell coolant from evaporator 250 passes through line 266 to coolant tank 268 which stores coolant for use in the cooling system used to remove excess heat from fuel cell 244. During steady operation, excess heat is removed from the coolant in air cooler 271, bypassing start-up furnace 276. Fuel for combustion chamber 202 leaves tank 264 through line 270 leading to combustor 202 through line 279. For start-up, a portion of the fuel is passed through line 270 to line 274 leading to start-up heater 276 while another portion passes to reformer combustion chamber 202 through line 279. Excess hydrogen contained in the exhaust from anode 242 was fed to combustion chamber 202

through line 280. Air for combustion chamber 202 is compressed by compressor 282 and passes to combustion chamber 202 through line 286. Air for start-up heater 276 passes through line 286. While air for combustion of methanol passes through line 278, coolant circulating through start-up heater 276 and line 262 raises fuel cell 244 to proper operating temperature upon start-up. In steady operation, hydrogen produced in reformer tubes 214 is converted to electricity in fuel cell 244, exhaust hydrogen from anode 242 of fuel cell 244 is used to supply fuel value to combustion chamber 202, while heat rejected from fuel cell 244 is used to vaporize the methanol water feed.

From the above description of suitable means for conducting the method of the present invention, it will be clear that various alternatives exist for maintaining the heat balance during the practice of the reforming process of the present invention when integrated with a phosphoric acid fuel cell system of the type hereinbefore described. The selection of a particular mode of operation will be dictated by overall process economics prevalent with any particular H₂-air fuel cell system and the desire to maximize the production of gaseous hydrogen while operating under the most beneficial conditions of temperature and pressure.

The following examples are offered for a better understanding of the reforming process of the present invention, but the invention is not to be construed as limited thereto.

Example I

A mixture of air and hydrogen was separately fed to a burner equipped with a heating coil of the type shown in Figure 1 of the drawings. In separate runs, a water/methanol feedstock at molar feed ratios of 4.5 and 9.0 was preheated to a temperature of 900°F in a mineral oil heated vaporizer 11. The preheated water/methanol

feedstock was passed into heating coil 13 of burner 14 and superheated to 900°F. The water/methanol feedstock exited the burner at 900°F and was passed into the inlet section of experimental subscale reformer 18 which consisted of a one-inch diameter pipe with a one foot long catalyst bed consisting of 206 grams of a ZnO/CuO combination catalyst on an alumina support. The composition of the catalyst of the type conventionally used for the water gas shift reaction comprised of 11.6% by weight Zn, 27.5% by weight Cu, and 29.9% by weight alumina. Reforming of the methanol in reformer 18 was accomplished at 14.7 psia and a constant weight hourly space velocity of 1.5 grams (gm) methanol feed/gm catalyst/hour. Steam reforming took place within the catalyst bed with the heat being provided directly thereto by the superheated gases flowing through reformer 18.

In both runs, effluent samples collected from condenser 20 and analyzed for CO content using a gas chromatograph indicated that the carbon monoxide level was below the calibration range of the gas chromatograph (100 - 200 ppm).

The methanol conversion for the 4.5 and 9.0 water/molar feed ratios in the two runs was 84.6 and 96.2% respectively. The first order rate constants overall were 2.8 and 4.9 hr^{-1} respectively. The projected weight hourly space velocities for the 4.5 and 9.0 water/molar feed ratios in the two runs to yield 99.8% methanol conversion was calculated to be 0.45 and 0.789 gm methanol feed/gm catalyst/hour respectively.

The temperature profile through the length of the reformer is shown in Table II below.

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Table II

Distance from Inlet of Catalyst <u>Bed (inches)</u>	Temperature of Bed (°F) H ₂ O/CH ₃ OH molar ratio	
	4.5	9.0
0	900	900
2	820	780
4	630	650
6	580	620
8	550	580
10	520	550
12	480	550
14	450	520

The gaseous product exiting the reformer was cooled, collected and analyzed with a gas chromatograph (G.C.) during the course of the reforming reaction. The conversion results are summarized in Table III below.

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Table III

in .).	H_2O/CH_3OH	Run Duration	% Conversion of Methanol		Gaseous Effluent Composition			
	Molar Ratio	(Hours)	Initial	Final	H_2	CO_2	CO	CH_4
	4.5	4.0	84.6	84.6	80.2	19.8	(1)	0.0
	9.0	4.0	96.2	96.2	72.75	27.25	(1)	0.0
control*	1.3	4.0	98.5	99.5	74.0	24.0	2.0	0.0

* Typical results from conventional steam reforming of methanol at 525°F reactant temperature.

(1) Less than G.C. detection, (100 - 200 ppm)

Example II

An experiment was conducted with a shell and tube type reactor in which the catalyst was divided into two sections. The first section extended six inches from the inlet of the 13 reactor tubes. The second catalyst section extended the remaining 18 inches of the tubes to the outlet. The first section contained a low activity, high temperature resistant catalyst consisting of 978.0 grams of a zinc-chromium oxide catalyst composed of 55.0% by weight Zn, and 22.0% by weight chromium oxide. The second catalyst section contained 5884.0 grams of a high activity, low temperature catalyst consisting of ZnO/CuO combination with an alumina support; the catalyst comprised 11.6% by weight Zn, 27.5% by weight Cu, and 29.9% by weight alumina and was of the type conventionally used for the water-gas shift reaction.

The water/methanol feedstock molar ratio was 2.0. Effluent samples collected from condenser 20 and analyzed for CO level indicated a concentration varying from 0.5 to 2.0 weight percent. The methanol conversion was 99.5%. The first order rate constant was 2.44 gm methanol feed/gm catalyst/hour. The weight hourly space velocity was 0.46 gm methanol feed/gm catalyst/hour.

The temperature profile through the length of the reformer is shown in Table IV below. This illustrates the effect of the upper, high temperature catalyst section in protecting the lower, low temperature catalyst from the high inlet temperatures necessary to complete the reaction with an optimally sized reactor.

→ Table IV

<u>Distance from Inlet of Catalyst Bed (inches)</u>	<u>Temperature of Bed (°F)</u>
<u>First Section</u>	
0.0	800.0
0.25	600.0
1.5	510.0
3.0	500.0
<u>Second Section</u>	
4.0	410.0
12.0	425.0
18.0	440.0
26.0	458.0

The conversion results are summarized in Table V below.

Table V

<u>% Conversion of Methanol</u>	<u>Gaseous Effluent Composition (Mole %)</u>			
Initial	Final	H ₂	CO ₂	CO
98.5	99.5	74.75	24.24	1.01
				0.0

Example III

A mixture of methanol and water containing 1.3 moles of water per mole of methanol was preheated to 385°F, then superheated to 720°F. Five thousand five hundred

(5500) ml/hr of the superheated mixture was passed through reformer tubes containing 6290 cc of a zinc oxide-copper oxide-alumina catalyst comprising 11.6 wt. % zinc, 27.5 wt. % copper and 29.2 wt. % alumina, having a specific gravity of 6050 g and a bulk density of 0.92 gm/cc. The space velocity within the reformer was therefore 0.469 hr^{-1} on a mass basis (g/hr of methanol/g of catalyst) or 985 hr^{-1} on the basis of volumes of H_2 in the feed per hour/catalyst volume. The reaction tubes were disposed within a shell heated by 14,000 g/hr of flue gases entering the shell at 890°F and leaving at 547°F yielding an average rate of heat input to the reformer of 5200 kcal/hr. The average catalyst bed temperature was 535°F, and the temperature of the reactants leaving the reformer was 565°F. The conversion of methanol was essentially completely converted yielding 8,185 l. of gas at STP per hour having a composition of 73.4 mole % H_2 , 24.0 mole % CO_2 and 2.6 mole % CO.

Example IV

The procedure of Example I was repeated in a single tube laboratory scale reformer 1 in. in diameter by 12 in. long maintained at 525°F using a volumetric space velocity of 836 hr^{-1} (cc of H_2 at STP per hour/cc of catalyst). The methanol conversion obtained was 98.48%. Analysis of the product gases indicated a composition of 74.8 mole % H_2 , 24.0 mole % CO_2 and 1.21 mole % CO.

While specific components of the present system are defined in the working examples above, many other variables may be introduced which may in any way affect, enhance or otherwise improve the present invention. These are intended to be included herein.

While specific components of the present system are defined in the working examples above, many other variables may be introduced which may in any way affect, enhance or otherwise improve the present invention. These are intended to be included herein.

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Although variations are shown in the present application, many modifications and ramifications may occur to those skilled in the art upon reading the present disclosure. These, too, are intended to be included herein.

CLAIMS

1. A process of providing a continuous supply of hydrogen fuel to a fuel cell system, the system being comprised of a heat exchanger, a burner, a catalytic reactor containing a catalyst bed for catalyzing the production of hydrogen from a gaseous mixture of water and methanol and a fuel cell comprised of a fuel electrode, an oxygen electrode and an electrolyte disposed therebetween, the process comprising the steps of:

(a) passing a gaseous mixture consisting essentially of water and methanol to the heat exchanger to heat the mixture to a superheated state, the temperature and composition of the superheated mixture being sufficient to supply at least about 90% of the heat required for reforming the methanol contained in said mixture by condensation,

(b) passing the superheated gaseous mixture of water and methanol into the catalytic reactor to form hydrogen by an endothermic reaction of water and methanol over the catalyst bed, the catalytic reactor being in the form of a tube having a length to diameter ratio of from about 2 to about 6, said catalyst bed comprising a low activity, high stability zinc oxide and chromium oxide catalyst comprised of about 30 to 65 percent by weight Zn and about 5 to 35 percent by weight Cr, followed by a high activity zinc oxide and copper oxide catalyst on alumina comprised of about 5 to 20 percent by weight Zn, about 15 to 40 percent by weight Cu, and about 15 to 50 percent by weight alumina, the temperature of said superheated mixture being between about 425° and about 600°C and the water to methanol ratio being between about 2 and about 9.

- (c) directing hydrogen produced in step (b) to the fuel electrode of the fuel cell,
- (d) directing air into the oxygen electrode of the fuel cell to effect an electrochemical reaction to produce electricity,
- (e) exhausting the gaseous effluent from the fuel electrode, a portion of which is a combustible gas, burning the combustible portion of the fuel electrode exhaust in the burner, feeding the burner exhaust to the heat exchanger to supply heat for the superheating of the water and methanol in step (a) whereby the gases exhausted from the fuel electrode supply at least a major portion of the thermal energy, via combustion, to heat the water/methanol mixture to the superheated state.

2. A process of providing a continuous supply of hydrogen fuel to a fuel cell system, the system being comprised of a heat exchanger, a burner, a catalytic reactor containing a catalyst bed for catalyzing the production of hydrogen from a gaseous mixture consisting essentially of water and methanol and a fuel cell comprised of a fuel electrode, an oxygen electrode and an electrolyte disposed therebetween, the process comprising the steps of:

- (a) passing a gaseous mixture of water and methanol to the heat exchanger to heat the mixture to a superheated state, the temperature and composition of the superheated mixture being sufficient to supply at least about 75% of heat required for reforming the methanol contained in said mixture by condensation,

- (b) passing the superheated gaseous mixture of water and methanol into the catalytic reactor to form hydrogen by an endothermic reaction of water and methanol over the catalyst bed, the catalytic reactor being in the form of a simple tube having a length to diameter ratio of less than about 10 to 1,
- (c) directing hydrogen produced in step (b) to the fuel electrode of the fuel cell,
- (d) directing air into the oxygen electrode of the fuel cell to effect an electrochemical reaction to produce electricity,
- (e) exhausting the gaseous effluent from the fuel electrode, a portion of which is a combustible gas, burning the combustible portion of the fuel electrode exhaust in the burner, feeding the burner exhaust to the heat exchanger to supply heat for the superheating of the water and methanol in step (a) whereby the gases exhausted from the fuel electrode supply the thermal energy, via combustion, to heat the water/methanol mixture to the superheated state.

3. The process of Claim 2 wherein a portion of the catalytic reactor exhaust is comprised of water which is condensed and recycled for use in the catalytic steam reforming reaction.

4. The process of Claim 2 wherein the water/methanol mixture is superheated to a temperature between about 800° and about 1100°F.

5. The process of Claim 2 wherein the water/methanol mixture is superheated to a temperature of about 850 to about 1000°F.

6. The process of Claim 2 wherein the water/methanol molar ratio in the superheated gaseous mixture is between about 2 to about 9.

7. The process of Claim 2 wherein the fuel cell electrolyte is phosphoric acid.

8. The process of Claim 2 wherein the catalyst in the catalyst bed is a combination of zinc and chromium oxides on alumina.

9. The process of Claim 2 wherein the catalyst bed comprises a low activity, high stability zinc oxide and chromium oxide catalyst comprised of about 40 to 65 percent by weight Zn and about 10 to 30 percent by weight Cr, followed by a high activity zinc oxide and copper oxide catalyst on alumina comprised of about 5 to 20 percent by weight Zn, about 20 to 35 percent by weight Cu, and about 20 to 40 percent by weight alumina.

10. A process of providing a continuous supply of hydrogen fuel to a fuel cell system, the system being comprised of a heat exchanger, a burner, a catalytic reactor containing a catalyst bed for catalyzing the production of hydrogen from a gaseous mixture consisting essentially of water and methanol and a fuel cell comprised of a fuel electrode, an oxygen electrode and an electrolyte disposed therebetween, the process comprising the steps of:

(a) passing a gaseous mixture of water and methanol to the heat exchanger to heat the mixture to a superheated state,

(b) passing the superheated gaseous mixture of water and methanol into the catalytic reactor to

form hydrogen by an endothermic reaction of water and methanol over the catalyst bed,

(c) directing hydrogen produced in step (b) to the fuel electrode of the fuel cell,

(d) directing air into the oxygen electrode of the fuel cell to effect an electrochemical reaction to produce electricity,

(e) exhausting the gaseous effluent from the fuel electrode, a portion of which is a combustible gas, burning the combustible portion of the fuel electrode exhaust in the burner, feeding the burner exhaust to the heat exchanger to supply heat for the superheating of the water and methanol in step (a) whereby the gases exhausted from the fuel electrode supply the thermal energy, via combustion, to heat the water/methanol mixture to the superheated state.

11. The process of Claim 10 wherein a portion of the catalytic reactor exhaust is comprised of water which is condensed and recycled for use in the catalytic steam reforming reaction.

12. The process of Claim 10 wherein the water/methanol mixture is superheated to a temperature between about 800° and about 1100°F.

13. The process of Claim 10 wherein the water/methanol mixture is superheated to a temperature of about 850 to about 1000°F.

14. The process of Claim 10 wherein the water/methanol molar ratio in the superheated gaseous mixture is between about 2 to about 9.

15. The process of Claim 10 wherein the fuel cell electrolyte is phosphoric acid.

16. The process of Claim 10 wherein the catalyst in the catalyst bed is a combination of zinc and chromium oxides on alumina.

17. The process of Claim 10 wherein the catalyst bed comprises a low activity, high stability zinc oxide and chromium oxide catalyst comprised of about 40 to 65 percent by weight Zn and about 10 to 30 percent by weight Cr, followed by a high activity zinc oxide and copper oxide catalyst on alumina comprised of about 5 to 20 percent by weight Zn, about 20 to 35 percent by weight Cu, and about 20 to 40 percent by weight alumina.

18. In a process for the production of hydrogen, said process comprising passing a gaseous feed mixture consisting essentially of methanol and water into a reactor over a catalyst bed, the improvement comprising superheating the gaseous mixture to a temperature between about 700° to about 1,100°F., and then feeding the superheated gaseous mixture to the reactor in contact with the catalyst bed contained therein, to produce hydrogen, at least a major portion of the heat for the catalytic reaction being extracted from the superheated gaseous mixture.

19. The process of Claim 18 wherein the catalyst bed is divided into a first section extending from the inlet of the reactor bed and a second section extending from the end of the first section to the outlet of the reactor bed, the first section containing a low activity, high temperature resistant steam reforming catalyst and the second section containing a high activity steam reforming catalyst.

20. The process of Claim 18 wherein the catalyst in the catalyst bed is a combination of zinc oxide and chromium oxide on alumina.

21. The process of Claim 19 wherein the low activity catalyst is a combination of oxides of zinc and chromium comprised of about 40% to 60% by weight Zn and about 10% to 30% by weight Cr and the high activity catalyst is a combination of oxides of zinc and copper on alumina comprised of about 5% to 20% by weight Zn, about 20% to 35% by weight Cu and about 20% to 40% by weight alumina.

22. The process of Claim 18 wherein the water/methanol molar ratio in the gaseous mixture is between about 1.0 to about 10.0.

23. The process of Claim 18 wherein the gaseous mixture is superheated to a temperature of about 850° to about 1,000°F.

24. An integrated methanol steam reformer, combustor chamber, and methanol superheater unit comprising:

means defining a combustion chamber having an inlet and an exhaust, said exhaust being connected to means defining a duct, superheater means for heating a mixture consisting essentially of methanol and water disposed within said combustion chamber, the outlet of said superheater means being operably connected to the inlet of a methanol heater/supply tube passing through said duct, a shell encompassing said duct adjacent said means defining a combustion chamber, said duct opening into the interior of said shell and a plurality of tubes operably connected to

said methanol heater/supply tube disposed within said shell exterior to said duct, said tubes having a catalyst for steam reforming of methanol into a hydrogen rich gas disposed therein.

25. The apparatus of Claim 24 further including:

a fuel cell comprising means defining an anode chamber and means defining a cathode chamber;

means for supplying hydrogen rich gas from said reformer to the anode chamber of said fuel cell;

means for recovering hydrogen from said anode chamber and employing said hydrogen to heat said mixture of methanol and water prior to its entry into said tubes disposed exterior to said duct; and

means for recovering and condensing water from the anode chamber of said fuel cell and employing said water for cooling of said fuel cell.

26. An integrated apparatus for the production of hydrogen and production of electricity therefrom comprising a reforming chamber having reforming catalyst disposed therein and means for supplying a superheated gaseous mixture consisting essentially of methanol and water to said reforming chamber at such a temperature that at least a major portion of the heat required for reforming said mixture is supplied by the heat contained within said gaseous superheated mixture, said temperature being between about 700° and 1100°F, a fuel cell comprising means defining an anode chamber and means defining a cathode chamber; means for supplying hydrogen rich gas from said reforming chamber to said anode chamber, and means for recovering hydrogen from said

anode chamber and employing said hydrogen to heat said mixture of methanol and water prior to its entry into said reforming chamber.

27. The apparatus of Claim 26 wherein the reforming chamber is divided into a first section extending from the inlet of the chamber and a second section extending from the end of the first section to the outlet of the chamber, the first section containing a low activity, high temperature resistant steam reforming catalyst and the second section containing a high activity steam reforming catalyst.

28. The apparatus of Claim 26 wherein the catalyst in the catalyst bed is a combination of zinc oxide and chromium oxide on alumina.

29. The apparatus of Claim 28 wherein the low activity catalyst is a combination of oxides of zinc and chromium comprised of about 40% to 60% by weight Zn and about 10% to 30% by weight Cr and the high activity catalyst is a combination of oxides of zinc and copper on alumina comprised of about 5% to 20% by weight Zn, about 20% to 35% by weight Cu and about 20% to 40% by weight alumina.

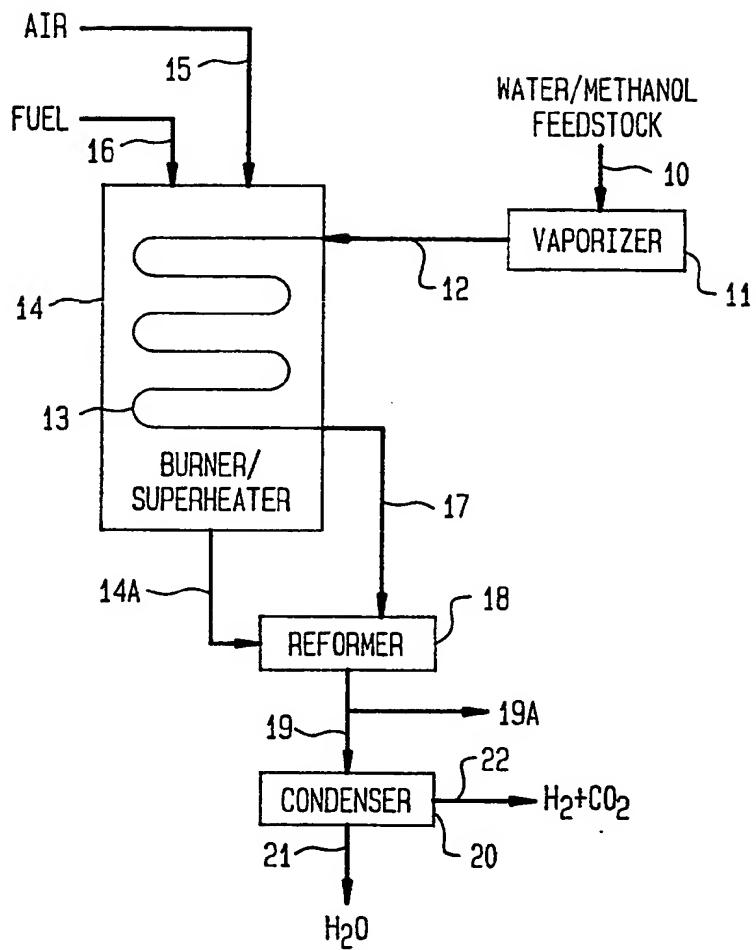
30. The process of Claim 26 further comprising means for maintaining the water/methanol molar ratio in the gaseous mixture between about 1.0 to about 10.0.

31. The apparatus of Claim 26 wherein the temperature at which the gaseous superheated mixture of methanol and water is supplied to said reforming chamber is between about 850° and 1100°F.

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FIG. 1



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FIG. 2

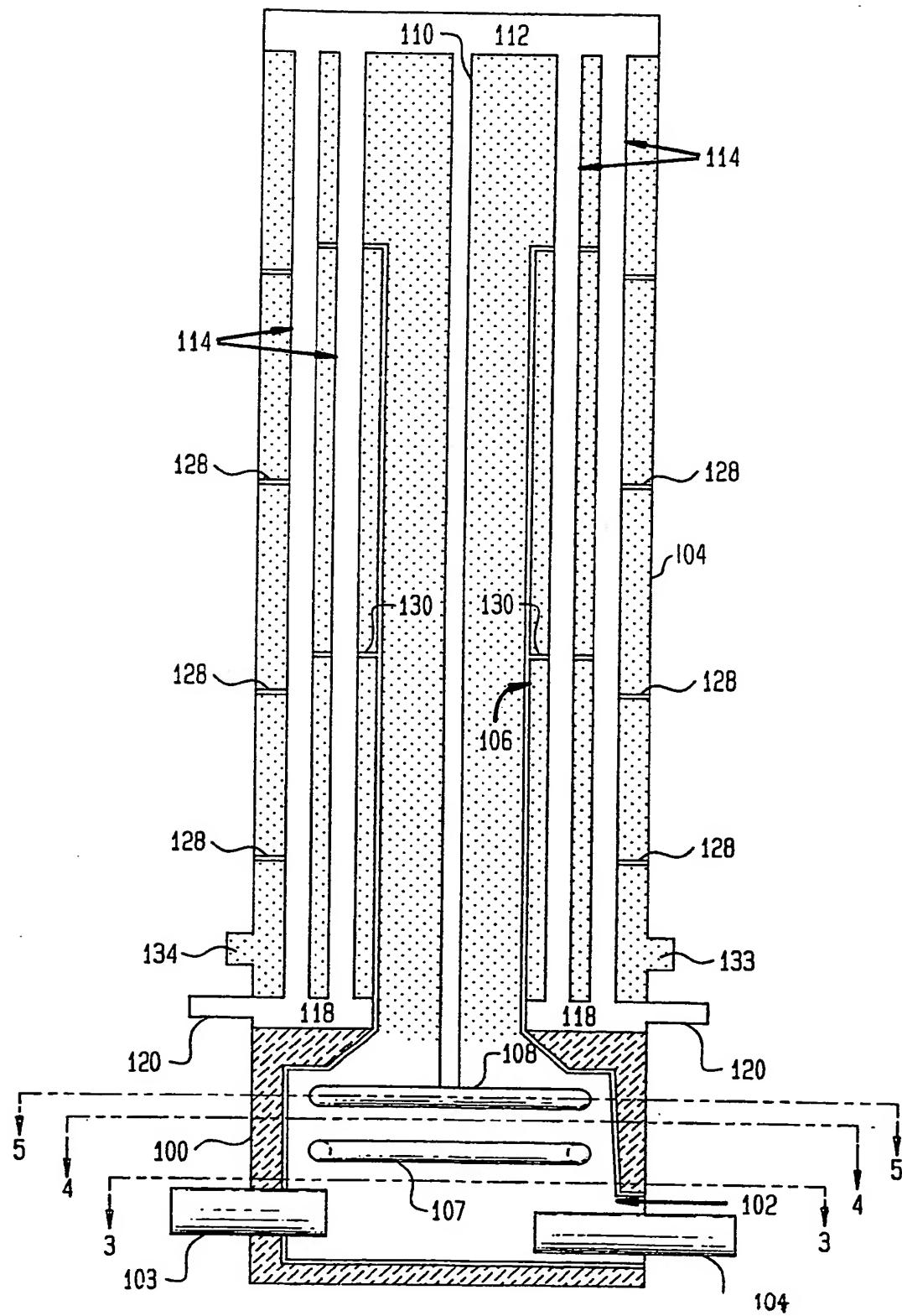
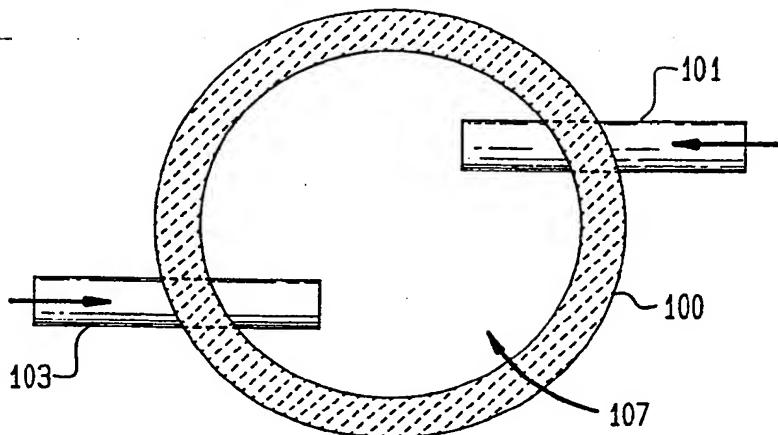
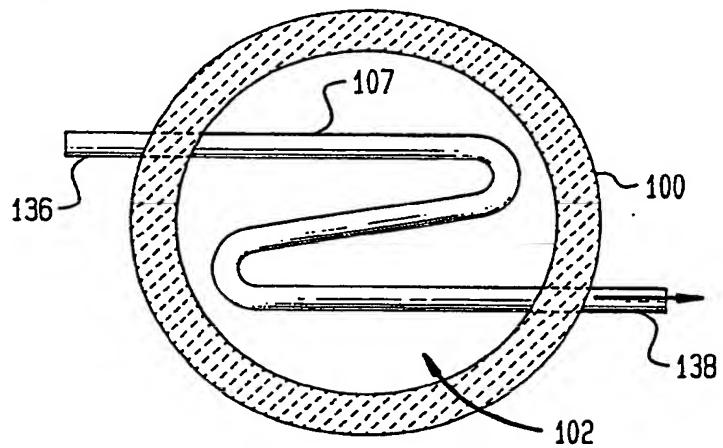
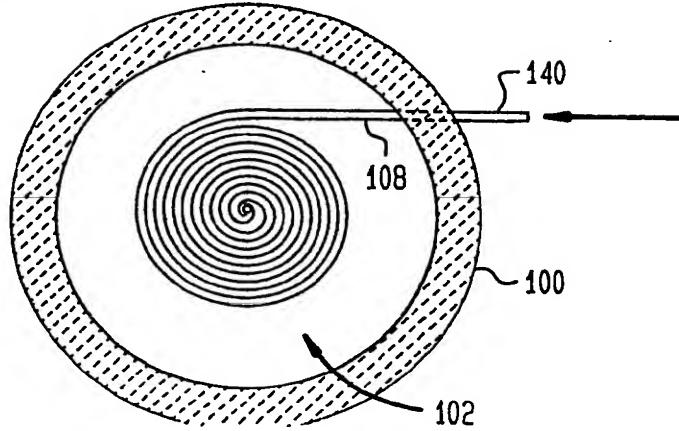
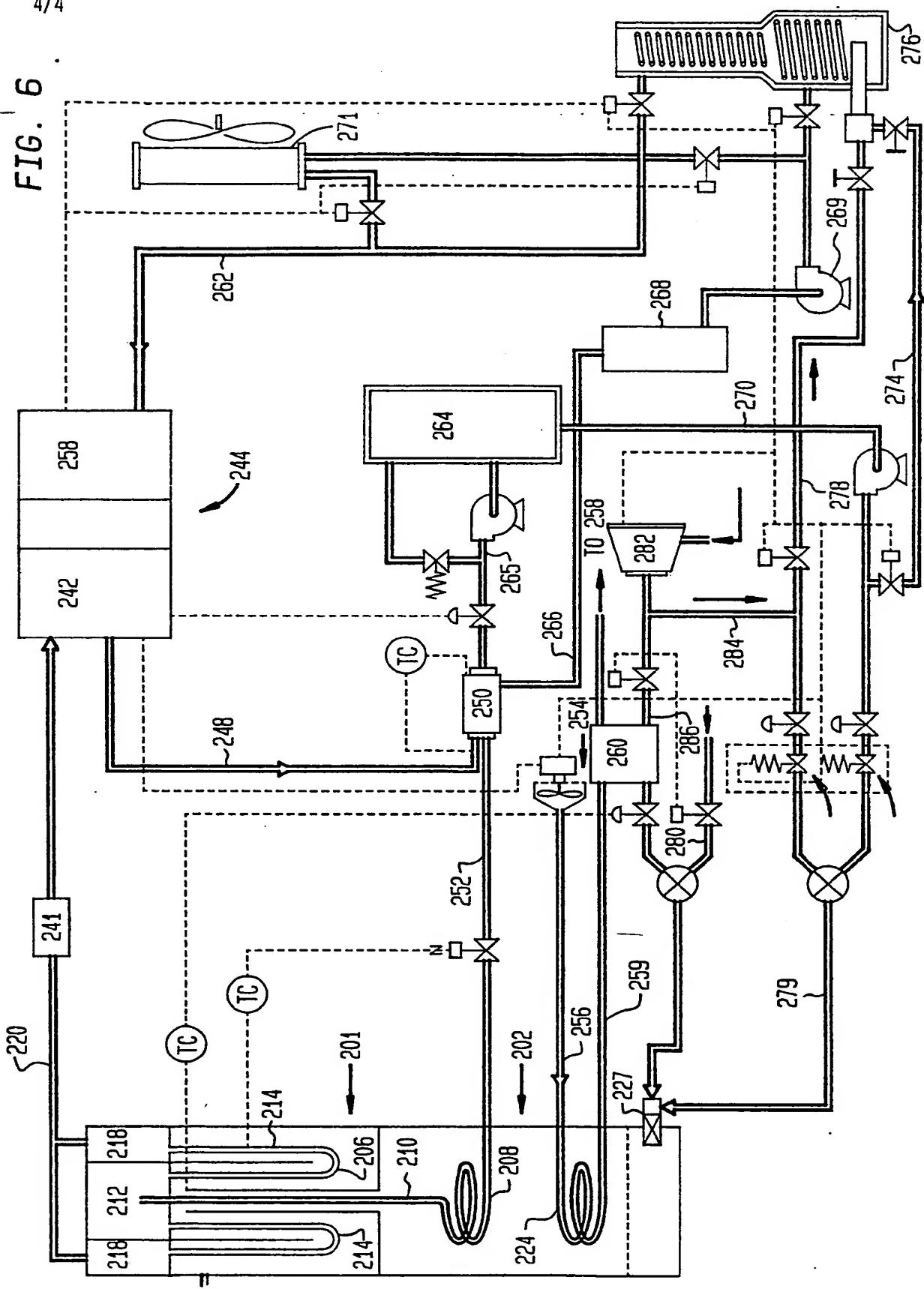


FIG. 3**FIG. 4****FIG. 5**

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FIG. 6





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C 01 B 3/32

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㉕ Applicant: ENGELHARD CORPORATION
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㉜ Fuel cell integrated with steam reformer.

㉝ A H₂-air fuel cell integrated with a steam reformer is disclosed wherein a superheated water/methanol mixture is fed to a catalytic reformer to provide a continuous supply of hydrogen to the fuel cell, the gases exhausted from the anode of the fuel cell providing the thermal energy, via combustion, for superheating the water/methanol mixture.

EP 0 206 608 A3



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EUROPEAN SEARCH REPORT

0206606

EP 86 30 4371

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	DE-A-2 640 456 (NISSAN MOTOR CO.) * Claims 1,3; page 1, paragraph 1; page 2, last paragraph - page 3, paragraph 1; page 6, line 8 - page 7, line 13; page 8, line 15 - page 9, line 6 *	18,19, 20,23	H 01 M 8/06 C 01 B 3/32
Y		1-7,9 15,22 26,27 28,30 31	
Y	US-A-3 469 944 (J.P. BOCARD et al.) * Column 3, lines 55-74; column 4, line 65 - column 5, line 11; claim 2; figure 1 *	1-7,9 15,22 26,27 28,30 31	TECHNICAL FIELDS SEARCHED (Int. Cl.4) H 01 M C 01 B
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The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-04-1987	D'HONDT J.W.	
CATEGORY OF CITED DOCUMENTS			
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Application number

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DOCUMENTS CONSIDERED TO BE RELEVANT			Page 2
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
Y	FR-A-1 553 361 (GENERAL ELECTRIC CO.) * Page 2, right-hand column, last paragraph - page 3, left-hand column, paragraph 3; page 5, right-hand column, paragraph 6 - page 6, left-hand column, paragraph 1; figure 5 *	1-7, 9-15, 22, 26, 27, 28, 30, 31	
X	EP-A-0 010 779 (METALLGESELLSCHAFT) * Claims 1,2 *	18, 19, 22, 23	
A	--- CHEMICAL ABSTRACTS, vol. 77, no. 2, 10th July 1972, page 166, left-hand column, abstract no. 7898x, Columbus, Ohio, US; H.J. HENKEL et al.: "Production of hydrogen by steam reforming", & JOURNEES INT. ETUDE PILES COMBUST., C. R., 3rd 1969, 273-9 * Whole abstract *	1	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
X	--- GB-A-2 135 295 (MITSUBISHI GAS CHEMICAL CO., INC.) * Page 1, lines 11-13; page 3, lines 7-15, examples 6,14 *	18, 19, 22	
	---	-/-	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-04-1987	D'HONDT J.W.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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A : technological background	D : document cited in the application		
O : non-written disclosure	L : document cited for other reasons		
P : intermediate document	& : member of the same patent family, corresponding document		



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Application number

EP 86 30 4371

DOCUMENTS CONSIDERED TO BE RELEVANT

Page 3

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
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X	BE-A- 657 241 (UNION CARBIDE CORP.) * Page 4, line 10 - page 5, line 3; page 7, last paragraph - page 8, paragraph 1; figure 1 *	2, 6, 10 , 14, 18 , 22	
A	EP-A-0 018 700 (METALLGESELLSCHAFT AG) * Claim 4 *	16, 17	
A	US-A-3 179 500 (M.D. BOWEN) * Figure 2; column 6, lines 65-69 *	24	
P, X	US-A-4 588 659 (S.G. ABENS et al.) * Figure 5; column 4, line 62 - column 5, line 28; column 5, lines 36-43 *	24	

The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	29-04-1987	D'HONDT J.W.	
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